Translation of Jpn. Pat. Appln. KOKAI Publication No. 2001-126761

1. Filling No.: Japanese Patent Application No. 11-304847
2. Filling Date: October 27, 1999
3. Applicant: MITSUBISHI CHEMICALS CORPORATION
4. KOKAI Date: May 11, 2001
5.
6. Request of Examination: Not filed
7. Int. Cl.^{7} & Jpn. Pat. Cl.:

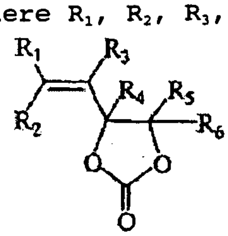
H01M 10/40	H01M 10/40	A5H029

Title of the Invention
Non-aqueous electrolytic solution type secondary battery

Abstract
[Object] To provide a non-aqueous electrolyte secondary battery having favorable battery characteristics, comprising non-aqueous solvent of relatively high flash point and relative dielectric constant of not smaller than 25 as main solvent.
[Means for Achieving the Object] A non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode, and a non-aqueous electrolytic solution having solute and non-aqueous solvent, in which the non-aqueous solvent contains 90% by weight or more of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, the flash point of the non-aqueous solvent is not lower than 70°C, and the nonaqueous solvent further contains at least one compound of vinylethylene carbonate.

Claims
[Claim 1] A non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode, and a non-aqueous electrolytic solution having solute and non-aqueous solvent, wherein the non-aqueous solvent contains 90% by weight or more of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, the flash point of the non-aqueous solvent is not lower than 70°C, and further the non-aqueous solvent contains at least one compound of vinylethylene carbonate expressed in the following general formula (I):
[Chem I]

where R_1, R_2, R_3, R_4, R_5, and R_6 each independently represent


(I)

a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. The non-aqueous electrolyte secondary battery according to claim 1, wherein the non-aqueous solvent consists of at least one compound of vinylethylene carbonate expressed in the general formula (I) and the solvent of relative dielectric constant of not smaller than 25 .

3. The non-aqueous electrolyte secondary battery according to claim 1 or 2, wherein the added amount of vinylethylene carbonate expressed in the general formula (I) is 0.01 to 10% by weight of the total amount of the non-aqueous solvent and vinylethylene carbonate expressed in the general formula (I).

4. The non-aqueous electrolyte secondary battery according to any one of claims 1 to 3, wherein the solvent of relative dielectric constant of not smaller than 25 is ethylene carbonate, propylene carbonate, butylene carbonate, γ-butyrolactone, and γ-valerolactone.

5. The non-aqueous electrolyte secondary battery according to any one of claims 1 to 4, wherein the negative electrode contains a carbon-based material capable of absorbing/releasing lithium.

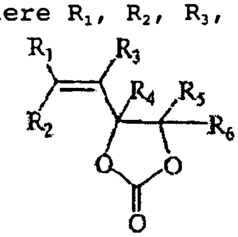
6. The non-aqueous electrolyte secondary battery according to any one of claims 1 to 5, wherein the negative electrode is a carbon-based material capable of absorbing/releasing lithium, or a mixture of the carbon-based material, and one or more types selected from the group consisting of lithium alloy and metal oxides capable of absorbing/releasing lithium.

7. The non-aqueous electrolyte secondary battery according to claim 5 or 6, wherein the carbon-based material is a graphite having a d value of 0.335 to 0.340 nm on a lattice plane (002 plane) as determined by X-ray diffraction.

8. A non-aqueous electrolyte for non-aqueous electrolyte secondary battery comprising a negative electrode and a positive electrode capable of absorbing/releasing lithium, wherein the non-aqueous solvent comprises solute and non-aqueous solvent, and the non-aqueous solvent contains 90% by weight or more of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, the flash point of the non-aqueous solvent is not lower than 70°C, and further the non-aqueous solvent contains at least one compound of vinylethylene carbonate expressed in the following general formula (I):

[Chem 2]

where R_1, R_2, R_3, R_4, R_5, and R_6 each independently represent



(I)

a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

Detailed Description of the Invention

[0001]

[Field of Industrial Use]

The present invention relates to a non-aqueous electrolyte secondary battery and a non-aqueous electrolytic solution used therein. More particularly, the invention relates to an improvement of a non-aqueous electrolyte secondary battery using an electrolytic solution containing vinylethylene carbonate of a specific composition and a specific non-aqueous solvent. According to the invention, in the secondary battery using the non-aqueous solvent of high relative dielectric constant, a secondary battery of high charging and discharging efficiency, excellent cycle characteristic, and high safety can be provided.

[0002]

[Prior Art]

With the recent trend for the reduction of weight and size of electrical appliances, there has been a growing demand for a lithium secondary battery having a high energy density. Further, with the expansion of the field to which the lithium secondary battery can be applied, it has been desired to further improve the battery performance. Extensive studies have been heretofore made of a secondary battery comprising metallic lithium as a negative electrode as a battery which can attain a high capacity. However, the greatest technical problem that prevents the practical use of such a secondary battery has been that when charge and discharge are repeated, metallic lithium grows in the form of dendrite and eventually reaches the positive electrode, causing shortcircuiting in the battery.

[0003]

To cope with this problem, a non-aqueous electrolyte secondary battery comprising as a negative electrode a carbon-based material capable of absorbing/releasing lithium such as coke, artificial graphite and natural graphite has been proposed. In such a non-aqueous electrolyte secondary battery, lithium doesn't exist in a metallic state, making it possible to inhibit the formation of dendrite and improve the battery life and safety. In particular, a non-aqueous electrolyte secondary battery comprising a graphite-based carbon material such as artificial graphite and natural graphite has been noted as one meeting the demand for higher capacity.

[0004]

In the lithium secondary battery using the carbon-based material, as the high dielectric constant solvent of non-aqueous electrolytic solution, usually, cyclic carbonates are widely used, such as propylene carbonate and ethylene carbonate. In the non-aqueous electrolyte secondary battery using non-graphite-based carbon material such as coke, a solvent containing propylene carbonate is

preferably used. On the other hand, in the non-aqueous electrolyte secondary battery using graphite-based carbon material alone or mixing another negative electrode material capable of absorbing/releasing lithium to form a negative electrode, by using a solvent containing propylene carbonate, decomposition reaction of propylene carbonate is promoted excessively on the electrode surface in charging operation, thereby disabling smooth absorbing/releasing of lithium on the graphite electrode.

[0005]

On the other hand, since ethylene carbonate is small in such decomposition, ethylene carbonate is widely used as solvent of high dielectric constant in the electrolytic solution of non-aqueous electrolyte secondary battery using a graphite-based negative electrode, but it is not sufficient for solving the problems of drop of cycle characteristic by decomposition of electrolytic solution. Further, ethylene carbonate exhibits a solidifying point as high as 36.4°C as compared with propylene carbonate and thus is not used singly but is used normally in admixture with a low viscosity solvent. For this reason, the electrolytic solution for lithium secondary battery comprising a graphite-based negative electrode normally comprises a mixed solvent of ethylene carbonate and diethyl carbonate. However, since most such low viscosity solvents normally have a low boiling point, it is disadvantageous in that when added in a large amount, the solvent exhibits a lowered flash point, though giving good electrolytic solution properties. On the contrary, when added only in a small amount, it is disadvantageous in electrical conductivity and viscosity at low temperatures.

[0006]

In this background, relating to a non-aqueous electrolyte battery using lithium metal as a negative electrode, Jpn. Pat. Appln. KOKAI Publication No. 4-87156 proposes an electrolytic solution using a compound having unsaturated carbon-carbon bond chain hardly reacting with lithium as solvent, for example, vinylethylene carbonate. However, since vinylethylene carbonate is used together with 1,2-dimethoxy ethane of low boiling solvent of equal volume, it does not solve the above problems.

[0007]

On the other hand, γ-butyrolactone, etc., which is a cyclic ester, has a high relative dielectric constant as well as a low solidifying point and thus can be used without being mixed with a low viscosity solvent. However, the γ-butyrolactone-based electrolytic solution, too, is subject to progress of decomposition of γ-butyrolactone on the surface of the graphite electrode during charge, causing deterioration of battery performance. Jpn. Pat. Appln. KOKAI Publication No. 11-31525 proposes an electrolyte solvent comprising as a main component γ-butyrolactone and as a subsidiary component ethylene

carbonate in an amount of from 15 to 35% by volume and practically comprising diethyl carbonate in an amount of not smaller than 16% by volume to inhibit the decomposition of γ-butyrolactone in a non-aqueous electrolyte secondary battery comprising a graphite-based carbon material as a negative electrode.

[0008]

[Object of the Invention]

However, the electrolytic solution proposed in the prior art has its effects, but further improvement is desired. It is hence an object of the invention to present a non-aqueous electrolyte secondary battery capable of exhibiting excellent battery characteristics even if using a non-aqueous solvent of relatively high flash point with relative dielectric constant of not smaller than 25 as the main solvent.

[0009]

[Means for Achieving the Object]

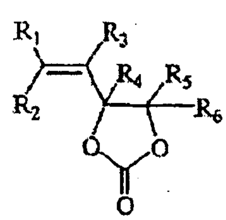
The present inventors have intensively studied to solve the problems, and completed the invention by discovering that the charging and discharging efficiency can be enhanced while improving the cycle characteristic and safety by using the solvent of electrolytic solution of a non-aqueous electrolyte secondary battery composed of a non-aqueous solvent containing 90% by weight or more of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, and adding at least one compound of vinylethylene carbonate having a specific structure to non-aqueous solvent having flash point of not lower than 70°C.

[0010]

That is, the invention presents a non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode, and a non-aqueous electrolytic solution having solute and non-aqueous solvent, in which the non-aqueous solvent contains 90% by weight or more of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, the flash point of the non-aqueous solvent is not lower than 70°C, and further the non-aqueous solvent contains at least one compound of vinylethylene carbonate expressed in the following general formula (I)

[0011]

[Chem 3]



(I)

[0012]
where R_1, R_2, R_3, R_4, R_5, and R_6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

The non-aqueous solvent used in the secondary battery of the invention is preferred to consist of at least one compound of vinylethylene carbonate expressed in the general formula (I) and the one or two or more solvents of relative dielectric constant of not smaller than 25.

[0013]

The added amount of vinylethylene carbonate expressed in the general formula (I) is 0.01 to 10% by weight of the total amount of the non-aqueous solvent and vinylethylene carbonate expressed in the general formula (I). More preferably, the negative electrode used in the secondary battery of the invention is preferred to contain a carbon-based material capable of absorbing/releasing lithium.

[0014]

[Embodiments of the Invention]

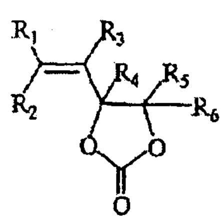
The non-aqueous electrolyte secondary battery of the invention is a non-aqueous electrolyte secondary battery comprising a negative electrode, a positive electrode, and a non-aqueous electrolytic solution having solute and non-aqueous solvent, in which the non-aqueous solvent contains 90% by weight of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, the flash point of the non-aqueous solvent is not lower than 70°C, and further the non-aqueous solvent contains at least one compound of vinylethylene carbonate expressed in the following general formula (I).

[0015]

The non-aqueous solvent of relative dielectric constant of not smaller than 25 used in the invention is not particularly specified, but preferred examples include ethylene carbonate, propylene carbonate, butylene carbonate, γ-butyrolactone, γ-valerolactone, sulforane, 3-methyl sulforane, and dimethyl sulfoxide, and in particular, ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolactone are preferred. These solvents may be used in combination of two or more types, and the combination is not particularly specified. Added to the non-aqueous solvent used in the present invention is a vinylethylene carbonate represented by the following general formula (I):

[0016]

[Chem 4]



(I)

[0017]
wherein R_1, R_2, R_3, R_4, R_5 and R_6 each independently represent a hydrogen atom or C_1-C_4 alkyl group. In the general formula (I), when R_1, R_2, R_3, R_4, R_5 and R_6 each are a C_1-C_4 alkyl group, specific examples of the C_1-C_4 alkyl group include methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, sec-butyl group, and tert-butyl group. Preferred among these alkyl groups are methyl group and ethyl group.

[0018]
Specific examples of the vinylethylene carbonate compound represented by the general formula (I) include 4-ethenyl-1,3-dioxolane-2-one (occasionally referred to as "vinylethylene carbonate"), 4-ethenyl-4-methyl-1,3-dioxolane-2-one, 4-ethenyl-4-ethyl-1,3-dioxolane-2-one, 4-ethenyl-4-n-propyl-1,3-dioxolane-2-one, 4-ethenyl-5-methyl-1,3-dioxolane-2-one, 4-ethenyl-5-ethyl-1,3-dioxolane-2-one, 4-ethenyl-5-n-propyl-1,3-dioxolane-2-one, etc.

[0019]
Among these vinylethylene carbonate compounds, 4-ethenyl-4-methyl-1,3-dioxolane-2-one is preferred, and vinylethylene carbonate is particularly preferred. They may be used in combination of two or more types. The added amount of vinylethylene carbonate used in the invention as expressed in the general formula (I) is preferably 0.01 to 10% by weight of the total amount of the non-aqueous solvent and vinylethylene carbonate expressed in the general formula (I), and more preferably 0.1 to 10% by weight, and further preferably 0.5 to 7% by weight.

[0020]
The non-aqueous solvent used in the invention contains 90% by weight of the solvent of relative dielectric constant of not smaller than 25. In the invention, the non-aqueous solvent is preferred to consist of the vinylethylene carbonate expressed in the general formula (1) and the solvent of relative dielectric constant of not smaller than 25. Further, in the foregoing embodiment of the invention, to the non-aqueous solvent having a relative dielectric constant of not smaller than 25 may be added one or more non-aqueous solvents other than mentioned above, e.g., dialkyl (preferably having from 1 to 4 carbon atoms) carbonate such as dimethyl carbonate, diethyl carbonate, di-n-propyl carbonate and ethylmethyl carbonate, cyclic ether such as tetrahydrofuran and 2-methyltetrahydrofuran, chain ether such as dimethoxyethane and dimethoxymethane, chain ester such as methyl acetate and ethyl propionate. In this case, these solvents may be added in such a combination that the flash point of the non-aqueous solvents, including those added, is not lower than 70°C.

[0021]
As the solute of the electrolytic solution to be used

in the invention, there may be used a lithium salt. The lithium salt is not specifically limited so far as it can be used as a solute. A specific example of such a lithium salt is an inorganic lithium salt selected from $LiClO_4$, $LiPF_6$ and $LiBF_4$ or a fluorine-containing organic lithium salt such as $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiN(CF_3CF_2SO_2)_2$, $LiN(CF_3SO_2)(C_4F_9SO_2)$ and $LiC(CF_3SO2)_3$. Preferred among these lithium salts are $LiPF_6$ and $LiBF_4$. Two or more of these solutes may be used in admixture.

[0022]

The molarity of the lithium salt as the solute in the electrolytic solution is preferably from 0.5 to 2 mol/l. When the molarity of the lithium salt falls below 0.5 mol/l or exceeds 2 mol/l, it is disadvantageous in that the electrolytic solution exhibits a low electrical conductivity that deteriorates the battery performance. The material of the negative electrode constituting the battery of the invention is not specifically limited so far as it contains a carbon-based material capable of absorbing and releasing lithium. Specific examples of such a carbon-based material include pyrolysis product of organic material obtained under various pyrolysis conditions, artificial graphite, natural graphite, etc. Preferred examples include artificial graphite manufactured by high temperature heat treatment of easily graphitizable pitch obtained from various materials, graphitized mesophase microbeads, graphitized mesophase pitch carbon fiber, other artificial graphite, refined natural graphite, or various surface treated graphitized material containing these types of pitch.

[0023]

However, these carbon-based materials preferably have a d value (interlaminar distance) of from 0.335 to 0.34 nm, more preferably from 0.335 to 0.337 nm on a lattice plane (002 plane) as determined by X-ray diffractometry according to the method of the Japan Society of Promotion of Scientific Research. These graphite materials preferably have an ash content of not greater than 1% by weight, more preferably not greater than 0.5% by weight, most preferably not greater than 0.1% by weight, and a crystalline size (Lc) of not smaller than 30 nm, more preferably not smaller than 50 nm, most preferably not smaller than 100 nm as determined by X-ray diffractometry according to the method of the Japan Society of Promotion of Scientific Research.

[0024]

The median diameter of carbon-based material is from 1 to 100 μm, preferably from 3 to 50 μm, more preferably from 5 to 40 μm, and most preferably from 7 to 30 μm as determined by the laser diffractometry/scattering method. The BET process specific surface area of the carbon-based material is preferably from 0.3 to 25.0 m^2/g, more preferably from 0.5 to 20.0 m^2/g, even more preferably from 0.7 to 15.0 m^2/g, and most preferably from 0.8 to 10.0 m^2/g. Moreover, the carbon-based material preferably

exhibits an intensity R (= I_B/I_A) of from 0 to 1.2 wherein I_A is the peak intensity in the range of from 1,580 to 1,620 cm^{-1} and I_B is the peak intensity in the range of from 1,350 to 1,370 cm-1 as determined by Raman spectroscopy, and a peak half width of not greater than 26 cm^{-1}, more preferably not greater than 25 cm^{-1} in the range of from 1,580 to 1,620 cm^{-1}.

[0025]

Further, the carbon-based material may be used in admixture with a negative electrode material capable of absorbing and releasing lithium. Examples of the negative electrode material capable of absorbing and releasing lithium other than carbon-based material include metal oxide material such as tin oxide and silicon oxide, metallic lithium, and various lithium alloys. Two or more of these negative electrode materials may be used in admixture. The process for the production of a negative electrode from these negative electrode materials is not specifically limited. The negative electrode can be produced, e.g., by optionally adding a binder, a thickening agent, an electrically-conducting material, a solvent, etc. to a negative electrode material to make a slurry, applying the slurry to a current collector substrate, and then drying the coated substrate. Alternatively, the negative electrode material may be rolled as it is to prepare a sheet-like electrode or may be compression-molded to prepare a pelletized electrode.

[0026]

The binder to be used in the production of the electrode is not specifically limited so far as it is a material inert to the solvent to be used in the production of the electrode and the electrolyte. Specific examples of such a material include polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, isoprene rubber, butadiene rubber, etc. Examples of the thickening agent include carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidized starch, phosphated starch, casein, etc. Examples of the electrically-conducting material include metallic material such as copper and nickel, and carbon-based material such as graphite and carbon black. As the material of the current collector for negative electrode, there may be used a metal such as copper, nickel and stainless steel. Preferred among these metals is a copper foil because it can be easily formed into a thin film and from the standpoint of cost.

[0027]

As the material of the positive electrode constituting the battery of the invention, there may be used a material capable of absorbing and releasing lithium such as lithium transition metal composite oxide material, e.g., lithium cobalt oxide, lithium nickel oxide and lithium manganese oxide. The process for the production of the positive electrode is not specifically limited. The

positive electrode can be produced according to the foregoing process for the production of the negative electrode. Referring to the shape of the positive electrode, a binder, an electrically-conducting material, a solvent, etc. may be optionally added to and mixed with the positive electrode material which is then applied to a current collector substrate to form a sheet electrode or press-molded to form a pelletized electrode. As the material of the current collector for positive electrode, there may be used a metal such as aluminum, titanium and tantalum or alloy thereof. Particularly preferred among these materials is aluminum or alloy thereof because it has a light weight and thus gives a high energy density.

[0028]

The material and shape of the separator to be used in the battery of the invention are not specifically limited. However, the separator is preferably selected from materials which are inert to the electrolytic solution and have excellent liquid retaining properties. A porous sheet or nonwoven cloth made of a polyolefin such as polyethylene and polypropylene as a raw material is preferably used.

[0029]

The process for the production of the battery of the invention having a negative electrode, a positive electrode and a non-aqueous electrolytic solution is not specifically limited but can be properly selected from those commonly employed. The shape of the battery is not specifically limited. A cylinder type obtained by spirally winding a sheet-like electrode and a separator, a cylinder type having an inside out structure comprising a pelletized electrode and a separator, a coin type having a pelletized electrode and a separator laminated on each other, etc. can be used.

[0030]

[Examples]

The present invention will be further described in the following examples and comparative examples, but the present invention should not be construed as being limited thereto so far as they fall within the scope of the invention.

(Example 1)

To 85 parts by weight of $LiCoO_2$ as a positive active material were added 6 parts by weight of carbon black and 9 parts by weight of a polyvinylidene fluoride KF-1000 (trade name; produced by Kureha Chemical Industry Co., Ltd.). The mixture was then dispersed with N-methyl-2-pyrrolidone to make a slurry. The slurry was uniformly applied to an aluminum foil having a thickness of 20 μm as a positive electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare a positive electrode.

[0031]

To 95 parts by weight of KS-44 (trade name; produced by TIMCAL, Ltd.), which is an artificial graphite powder

having a d value of 0.336 nm on a lattice plane (002 plane) as determined by X-ray diffractometry, a crystalline size (Lc) of not lower than 100 nm (264 nm), an ash content of 0.04% by weight, a median diameter of 17 μm as determined by the laser diffractometry/scattering method, a BET process specific surface area of 8.9 m^2/g, an intensity R (= I_B/I_A) of 0.15 wherein I_A is the peak intensity in the range of from 1,580 to 1,620 cm^{-1} and I_B is the peak intensity in the range of from 1,350 to $1,370^{-1}$ cm as determined by Raman spectroscopy that uses argon ion laser beam, and a peak half width of 22.2 cm^{-1} in the range of from 1,580 to 1,620 cm^{-1} were added 5 parts by weight of polyvinylidene fluoride. The mixture was then dispersed with N-methyl-2-pyrrolidone to make a slurry. The slurry thus made was uniformly applied to a copper foil having a thickness of 18 μm as a negative electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare a negative electrode.

[0032]

An electrolytic solution was prepared by dissolving a vinylethylene carbonate in a 1 : 1 (by volume) mixture of propylene carbonate and ethylene carbonate in a proportion of 3% per 97% by weight, and then dissolving dried lithium hexafluorophosphate ($LiPF_6$) as a solute in the solution in an amount of 1 mol/l in dried argon atmosphere. By using these positive electrode, negative electrode and electrolytic solution, the positive electrode was then received in a stainless steel can which also acts as a positive electrode conductor, and the negative electrode was then put on the positive electrode with a polyethylene separator impregnated with the electrolytic solution interposed therebetween. The can was then caulked with a sealing plate which also acts as a negative electrode conductor with an insulating gasket interposed therebetween to seal the can. Thus, a coin type battery was prepared.

[0033]

(Comparative Example 1)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving $LiPF_6$ in a 1 : 1 (by volume) mixture of propylene carbonate and ethylene carbonate in an amount of 1 mol/l was used.

[0034]

(Example 2)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving a vinylethylene carbonate in a 1 : 1 (by volume) mixture of ethylene carbonate and γ-butyrolactone in a proportion of 3% per 97% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

[0035]

(Comparative Example 2)

A coin type battery was prepared in the same manner

as in Example 1 except that an electrolytic solution prepared by dissolving $LiPF_6$ in a 1 : 1 (by volume) mixture of ethylene carbonate and γ-butyrolactone in an amount of 1 mol/l was used.

[0036]

(Example 3)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving a vinylethylene carbonate in a 1 : 1 mixture (by volume) of propylene carbonate and γ-butyrolactone in a proportion of 3% per 97% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

[0037]

(Comparative Example 3)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving $LiPF_6$ in a 1 : 1 mixture (by volume) of propylene carbonate and γ-butyrolactone in an amount of 1 mol/l was used.

[0038]

(Example 4)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving a vinylethylene carbonate in a propylene carbonate in a proportion of 3% per 97% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

[0039]

(Comparative Example 4)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving $LiPF_6$ in propylene carbonate in an amount of 1 mol/l was used.

[0040]

(Example 5)

A coin type battery was prepared in the same manner as in Example 1 except that an electrolytic solution prepared by dissolving a vinylethylene carbonate in a 1 : 1 mixture (by volume) of propylene carbonate and ethylene carbonate in a proportion of 5% per 95% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used. The batteries prepared in Examples 1 to 5 and Comparative Examples 1 to 4 were then subjected to cycle life test involving charge with a constant current of 0.5 mA to a termination voltage of 4.2 V and discharge to a termination voltage of 2.5 V at 25°C.

[0041]

The electrical conductivity of the electrolytic solutions used in Examples 1 to 5 at 20°C and -30°C are set forth in Table 1. For the measurement of electrical conductivity, an electrical conductivity meter (CM-30S, produced by DKK-TOA CORPORATION) was used. The flash point

was measured according to JIS K-2265. The discharge capacity per weight of negative electrode and charge-discharge efficiency at the 1st cycle of the various batteries are set forth in Table 2. The charge-discharge efficiency was determined by the following equation.

[0042]

[Formula 1]

Charge-discharge efficiency (%) = [(Discharge capacity)/(Charge capacity)]] × 100

[0043]

As shown in Tables 1 and 2, Comparative Examples 1, 3 and 4 underwent violent decomposition of electrolytic solution and thus didn't act as battery. On the other hand, the electrolytic solutions of the examples of the invention didn't solidify even at -30°C and exhibit a relatively high conductivity and thus provide an excellent capacity and charge-discharge efficiency when used in battery.

[0044]

[Table 1]

	Electrical conductivity (mS/cm)		Flash point (°C)
	20°C	-30°C	
Example 1	6.2	1.1	140
Example 2	9.1	2.6	119
Example 3	8.1	2.3	119
Example 4	5.3	1.0	138
Example 5	6.1	1.0	140

[Table 2]

	Capacity at 1st cycle (mAh/g)	Efficiency at 1st cycle (%)
Example 1	226	81.3
Example 2	230	83.0
Example 3	213	81.1
Example 4	198	78.1
Example 5	233	84.4
Comparative example 1	-	-
Comparative example 2	120	34.4
Comparative example 3	-	-
Comparative example 4	-	-

[0046]

[Advantages of the Invention]

The non-aqueous electrolyte secondary battery of the invention contains 90% by weight or more of one or two or more solvents selected from the solvents of relative dielectric constant of not smaller than 25, and further contains a non-aqueous solvent having flash point of not

lower than 70°C, and therefore the safety is high, the charging and discharging efficiency is high, and the cycle characteristic is excellent. Further the secondary battery of excellent cycle characteristic and storage characteristic at high temperature can be manufactured.